Using different analytical techniques to study beach rocks of Tamilnadu, India

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Abstract Beach rocks samples were collected from South East Coast of Tamilnadu, India. The mineralogical composition was determined using FT-IR and XRD. The natural radioactive measurements to detect radioactive elements were determined by gamma ray spectrometer. The multi-element analyses were carried out by INAA (Instrumental neutron activation analysis), with the standard Estuarine Sediment as reference material. The geochemical behavior of elements in the region is discussed. The occurrence of the radioactive and non-radioactive elements is discussed for their geological significance. The results were used to assess environmental toxicity of heavy metals and radiation hazard in the study area.

Key words Beach rock, FT-IR, XRD, INAA(Instrumental neutron activation analysis), Natural radioactivity, Gamma spectrometry, Multi-element analysis

1 Introduction

Beach rock, a peculiar rock formations, is commonly found along tropical and subtropical coasts^[1-3]. As a layer deposit inclined towards the sea, it is a sedimentary formation indurate by the effects of carbonate cement-aragonite or magnesium calcite formed in the laver in the intertidal zone. Beach rock also acts as resistant barrier to erosion, thus affecting the shoreline's rate of erosion and overall developments. In India, such a formation is found along the South East Coast of Tamilnadu^[4]. Beach rock samples were collected from 15 sites from Rameshwaram to Kanyakumari of the coast covering around 360 km (Fig.1), for extensive investigation on its formation^[5-7]. The qualitative mineral analysis was carried out using FT-IR and XRD. The radioactive elements was analyzed by γ -ray spectrometer and the elemental composition by instrumental neutron activation analysis (INAA). This work is to assess one approach in order to ascertain whether heavy metals content may be identified from geochemical background by studying relationships among chemical and mineralogical properties of beach rocks, in addition to identifying areas with high natural radiation levels and evaluating potential risk and natural radiation dose surveys in mineral prospecting especially for uranium and thorium.

2 Materials and methods

2.1 Sample collection and preparation

From the sampling sites, approximately 1 kg sample was taken from the same rock and collected in a plastic bag. The samples were cleaned. The weathered surface was removed. The fresh materials were crushed, powdered using an agate mortar, dried for 24h at 110°C, and pulverized to particle sizes not greater than 2 mm mesh screen^[8].

2.2 FT-IR analysis

The major and minor minerals were qualitatively de termined by FT-IR (Nicolet Avator 360, at Annamalai University, Annamalainagar, Tamilnadu, India). Sample of 2 mg was mixed with 40 mg of spectroscopic KBr using a mortar and pestle. The FT-IR spectra were taken in 4000~400 cm⁻¹. The instrument scanned the spectra 16 times in 1 minute and the resolution was 5cm⁻¹.

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Fig.1 Location map.

2.3 XRD analysis

The samples were examined at room temperature by X-ray diffractrometer (D500, Siemens) having a curved graphite crystal diffracted monochromator, with Cu K α ray. A narrow slit of 0.1 mm was used with a scanning speed of 0.5° per minute and time constant of 2 s. The XRD patterns were obtained over the 2θ values in $20^{\circ} \sim 80^{\circ}$.

2.4 Radioactivity analysis

Selected amount of samples were packed in plastic containers and aged for 4 weeks to allow the parent nuclides in the samples to reach equilibrium with their respective progeny^[9]. The gamma spectra were collected for 20000 s. A $3" \times 3"$ NaI (Tl) detector was employed with adequate lead shielding to reduce the background by a factor of about 95%. The efficiency for various energies was arrived at using IAEA standard sources and required geometry. The concentra-

tions of various nuclides of interest are determined in $Bq\cdot kg^{-1}$. The peaks corresponding to 1.46 MeV (⁴⁰K), 1.76 MeV (²¹⁴Bi) and 2.614 MeV (²⁰⁸Tl) were used to detect the activity levels.

2.5 Ambient survey

At each sampling spot the ambient gamma dose was measured using a digital environmental radiation dosimeter (ERDM) with a GM tube. The ERDM was calibrated regularly using a standard source. The ERDM readings were recorded at 1 m above ground level. Five readings were taken at each spot and the average was recorded. The dose rates (Gy·h⁻¹) deduced from the activity values from the spectra were converted by D= (0.662 C_{Th} + 0.427 C_{U} + 0.043 C_{K}), where C_{Th} , C_{U} and C_{K} are the activity concentrations (Bq·kg⁻¹) of primordial radio nuclides ²³²Th, ²³⁸U and ⁴⁰K, respectively. The results are presented in Table 1.

Samples	Name of the sites	Activity concentration /Bq·kg ⁻¹			Absorbed dose rate /Gy·h ⁻¹		
		²³² Th	²³⁸ U	40 K	Calculated	Observed	
S_1	Rameswaram	10.11	BDL*	102.68	10.71	8.65	
S_2	Pampan	35.44	9.45	445.57	45.19	32.25	
S ₃	Mandapam	29.58	8.56	182.65	29.94	20.45	
S_4	Pudumadam	24.56	BDL	230.68	25.22	17.85	
S_5	Keelakarai	22.11	6.12	327.96	30.49	28.48	
S_6	Valinockam	55.56	13.68	226.14	50.18	40.18	
S_7	R. Vembar	38.65	10.89	397.26	45.81	35.78	
S_8	Sippikulam	324.15	86.28	130.00	244.38	184.98	
S ₉	Veerapandia pattanam	142.0	34.00	185.16	110.95	86.15	
S_{10}	Tiruchendur	170.90	33.45	227.57	130.54	110.26	
S_{11}	Manapad	221.40	58.56	273.21	174.69	155.27	
S ₁₂	Ovari	88.48	16.14	371.16	77.97	75.17	
S ₁₃	Idinthiakarai	250.49	52.34	400.57	195.63	165.15	
S ₁₄	Perumnal	389.56	88.00	164.98	287.37	254.57	
S ₁₅	Vattakottai	767.00	114.00	443.00	545.57	484.44	
_	Average	171.33	35.43	273.90	134.64	113.30	

Table 1 The activity concentration of ²³²Th, ²³⁸U and ⁴⁰K in beach rock samples from South East Coast of Tamilnadu, India

*Note: BDL –Below detectable limit.

2.6 INAA analysis

2.6.1 Sample irradiation and counting

Polypropylene tubes containing the sample and the gold as the standard for quantitative analysis were irradiated by thermal neutrons $(10^{11} \text{ cm}^{-2} \cdot \text{s}^{-1})$ in the KAMINI research reactor, Kalpakkam, Tamilnadu, India. To assay the short and long-lived radionuclides, two sets of irradiation, 5 min and 5 h, were performed. The samples of 5-min irradiation were counted for 100~300 s after 10 min cooling for the determination of ²⁸Al, ²⁷Mg, ⁴⁹Ca, ⁵¹Ti and ⁵²V, and a cooling of 200~300 min for ¹⁶⁵Dy, ⁵⁶Mn and ²⁴Na. The samples of 5-h irradiations to determine the medium and long-lived radionuclides (⁴²K, ⁵¹Cr, ⁵⁹Fe, ⁶⁰Co, ⁹⁵Zr, ¹⁴⁰La, ¹⁴¹Ce, ¹⁵²Eu, ¹⁵³Sm, ¹⁷⁵Yb and ¹⁸¹Hf) were counted for 10,000~30,000 s after a cooling time of 2, 4~7 and 35~50 d.

2.6.2 Radioactive assay

After irradiation the samples and standards were washed, wiped and mounted on standard Perspex plates. Samples were assayed for γ -activity of the activation products using an 80 cm³ HPGe detector coupled to a PC-based 4K analyzer in an efficiency-calibrated position with reproducible sample-to-detector geometry. The sample- to-detector distance was at 12~15 cm depending upon the level of activity to avoid true coincidences effects. The detec-

tor system had a resolution of 1.8 keV at 1332 keV. The activities of radionuclides were considered as a function of time to ensure purity and identity. Gamma-ray standard of 152 Eu was used for efficiency calibration of the detector.

2.6.3 Calculations

Peak areas corresponding to different photo peaks, after subtracting the linear Compton background, were converted to specific count rate (A_{sp}) by $A_{sp}=P_A/SDCW$, where P_A =peak area, S=saturation factor, C=counting correction, D=decay correction, and W=weight of the sample.

The concentration of the *i*th element (in µg/g) was calculated by Conc=[$A_{sp}/(A^*_{sp}K_{anal})$], where A_{sp} = specific count rate corrected per gram of the sample, A^*_{sp} =specific count rate of ¹⁹⁸Au, and $K_{anal} = K_0$ [($f+Q_0(\alpha)$) / ($f+*Q(\alpha)$)] · (ξ/ξ^*), where ξ is the detection efficiency of the detector for the γ -ray energy used, f is the sub-cadmium to epi-cadmium neutron flux ratio, and ratio of cross sections is $Q_0(\alpha)=I_0(\alpha)/\sigma_{th}$, where $I_0(\alpha)$ is the infinitely dilute resonance integral corrected for the non-ideal epithermal neutron flux distribution. Validation for the experimental setup was done by irradiating the Standard Reference Material (SRM 1646a estuarine sediment) for the same period of time in the same location of the reactor. The SRM analysis agreed well with the certified values.

3 Results and discussions

3.1 FT-IR analysis

The IR absorption peaks were compared with available literature. The minerals were identified as quartz, orthoclase, albite, kaolinite, montmorllinite, illite, calcite, aragonite, dolomite, ilmenite and rutile^[10-12]. Calcite and quartz are considered as major mineral from the IR absorption peaks.

3.2 XRD analysis

Qualitative mineralogy of the beach rock samples was determined with the standard interpretation procedures of XRD. Quartz, albite, orthoclase, kaolinite, calcite, aragonite, ilmenite, rutile and almandine garnet were identified from the peaks in diffractrogram. Major minerals in the samples are quartz and calcite. The presence of heavy minerals (ilmenite, garnet, rutile etc.,) may be the contribution from the hinterland geology, laterization of gneissose rocks, occurrence of small streams and categorization by waves and tides. The FT-IR findings are confirmed by XRD analysis and it reveals that these techniques are used for mineral analysis.

Therefore, there is a need to identify the regions where the metal content is supplemented by additions of contamination inputs, to identify areas with high natural radiation levels, and to evaluate potential risk and natural radiation dose surveys.

3.3 Radioactivity analysis

The distribution of natural radio nuclides in beach rock samples at 15 sampling sites and the corresponding absorbed dose rate in air above the ground level are presented in Table 1. The activities of 232 Th, 238 U and 40 K were averaged at 171.33 (10.11 ~ 767), 35.43 (BDL ~ 114) and 273.90 (102.68 ~ 443) Bq·kg⁻¹, respectively. Comparing with the world average of 30, 35 and 400 Bq·kg⁻¹ for 232 Th, 238 U and 40 K, respectively ^[13], the 232 Th was higher by a factor of 5.71, the 238 U activity was about the same, and 40 K activity was lower by a factor of 0.68. The high 232 Th activity found in the present study is due to the presence of monazite in the study area, as confirmed by XRD.

The 232 Th activity was higher at some places like Vattakottai (S₁₅), Perumanal (S₁₄), Idinthakkarai (S₁₃),

Manappad (S_{11}) and Sippikulam (S_8) . This may be due to the occurrence of radioactivity placer mineral in South West beach of Kerala. One can expect that during the South West monsoon the wind and torrential rain cause not only the displacement of thorium and uranium minerals but also all types of heavies to reach the sea by the process of erosion. The underwater current extends from Kerala in Arabian Sea extends up to Rameswaram via Kanyakumari in Bay of Bengal. This coastal configuration and current patterns may be considered to play a more vital role in the concentration of uranium and thorium bearing minerals which may be found apparently to decrease from Vattakottai to Rameswaram. A another possible explanation of higher thorium activities in some places may be drawn due to monazite deposit in the coastal places of Tamilnadu and Kerala which are due to weathering of rocks in Nilgiri hills and Western Ghat

3.4 Dose calculation

From Table 1, the calculated total absorbed dose rate due to the presence of Th²³², U²³⁸and K⁴⁰ in beach rock samples varied between 10.71 (Rameswaram) and 545.57 nGy·h⁻¹ (Vattakkottai). The mean absorbed dose rate 134.64 nGy·h⁻¹ was higher than the global background dose in air (59 nGy·h-1) complied by UNSCEAR^[13]. The observed and calculated dose rates are not always the same. The difference in the rates may be due to several reasons: (1) the ERDM may not practically be possible to maintain at the same levels at all sites, (2) the contribution from radon to the external exposures is not taken into account and (3) the secondary cosmic rays may enhance the reading in the ERDM. However, the absorbed dose rate value is lower in the study area compared to some of the higher background areas like Ramasar and Mahallat (190~ 8600 nGv· h^{-1}) in Iran, the South West Coast of India (1500 nGy· h^{-1}), Nieue Island of Pacific (1,100 nGy· h^{-1}) and in mines of Gerais in Brazil (2300 nGy·h⁻¹)^[14].

3.5 INAA analysis

The elemental contents in the beach rock samples are reported in Table 2. The calcium is the highest of all the elements in almost all the samples. This is due to high abundance of calcium carbonate in tropical and subtropical areas of ocean^[15] and also typical beach

rock formation^[16]. The highest Al content at S_{13} indicates the higher degree of weathering and reflects the degree of influence of sediment, whereas the lowest Al

content at S_1 implies the finer nature of sediment containing clay minerals and iron oxides^[17].

Elements	S_1	S_2	S ₃	S_4	S_5	S ₆	S_7	S_8	S ₉	S ₁₀	S ₁₁	S ₁₂	S ₁₃	S ₁₄	S ₁₅
Al /%	0.15	1.2	1.3	2.4	0.61	3.18	2.03	2.33	1.43	2.25	1.68	2.23	7.73	0.72	3.42
Mg /%	0.70	0.88	3.04	1.13	2.63	1.32	2.55	3.20	2.20	2.27	0.73	1.22	3.21	0.70	2.48
K /%	0.46	0.69	0.71	ND	0.79	1.89	1.22	ND	1.04	1.06	0.52	1.44	4.61	0.43	0.66
Na /%	0.42	0.57	0.43	0.52	0.39	0.85	0.59	0.15	0.51	0.44	0.43	0.96	1.79	0.22	0.52
Ca/ %	15.83	22.44	17.99	24.28	18.53	15.31	18.14	12.18	14.24	23.59	24.69	18.22	10.87	20.52	4.43
Ti /%	0.07	1.20	0.49	ND	0.04	0.34	0.12	7.04	0.06	ND	0.52	0.38	0.30	0.16	15.66
Fe/ %	0.81	2.37	2.48	0.29	0.33	1.39	0.67	15.83	0.44	0.61	0.73	1.13	5.45	0.51	23.12
Co/10 ⁻⁶	3.91	7.07	9.58	2.99	4.99	9.06	5.5	30	7.2	2.78	3.57	3.26	14.83	6.64	45.85
Cr/10 ⁻⁶	14.94	26.1	53.95	ND	21.75	36.31	102.84	187	29.48	55.58	38.28	25.95	97.2	54.39	304
V/10 ⁻⁶	4.76	62.6	37.82	5.66	5.87	20.25	13.31	416.2	15.68	72.45	30.97	27.98	62.87	11.87	631.9
Hf/10 ⁻⁶	5.21	17.24	26	2.24	3.81	14.78	9.14	56.28	5.63	6.88	45.43	20.25	14.73	4.56	101.4
Zr/10 ⁻⁶	ND*	ND*	2348	ND*	ND*	ND*	1612.24	2662	ND*	1087	1990	1525	1532	1027	4692
Mn/10 ⁻⁶	167.5	407.5	385.9	215.5	146.9	686.5	226.36	2809	778.84	499.4	114.1	139.8	580.3	432.2	2514
La/10 ⁻⁶	101.0	78.58	27.14	16.05	9.49	38.22	16.58	140	10.06	25.14	121.1	131.5	56.80	29.94	678.0
Ce/10 ⁻⁶	18.14	137.7	37.32	29.17	16.57	87.29	57.87	221.9	19.48	77.22	225.3	247	86.43	51.29	1288
Sm/10 ⁻⁶	1.10	5.62	2.49	1.64	1.05	3.08	1.22	11.05	0.95	3.80	11.06	12.33	4.07	2.43	60.36
Eu/10 ⁻⁶	0.49	1.06	2.21	0.74	0.80	2	0.96	2.85	0.84	0.68	1.35	1.34	2.56	0.55	5.69
Tb/10 ⁻⁶	0.30	0.99	0.41	0.18	0.16	0.74	0.22	1.25	0.45	0.67	0.98	1.25	2.80	0.6	7.21
Yb/10 ⁻⁶	0.44	0.19	0.65	0.41	0.22	0.824	0.49	2.61	0.56	0.89	1.35	2.81	4.79	1.08	14.08

*Note: ND - Not determined.

The higher Na and K contents at S₁₃ may be due to the extraction of sodium from rock during weathering, its absolute amount decreasing in the hydrolyzate sediments, whereas potassium first goes into solution but does not remain dissolved thus absorbed by the clay content^[18]. The difference in the behavior of Na and K during the weathering is due to the greater resistance of potash feldspar as compared with that of plagioclase feldspar^[19]. The variation in the distribution of Ca, Mg, Na and K in some locations may be mainly controlled by clay minerals in the study area. Nelson^[20] has pointed out that in the processes of ion exchange, the common ions inherited from soil environment (Ca²⁺ and H⁺) by the absorption in surface particles are replaced by most abundant ions (Na⁺ and $Mg^{+})^{6}$. The net reaction between fluvial clays and seawater is primarily an exchange of seawater Na for bound Ca⁺. The higher Na and Mg concentrations at S_{13} may be due to the low Ca content in the marginal environment such as tidal channel and, swamps can also be attributed to the above replacement of Ca by other ions^[21].

The lowest and highest concentration of Fe, Ti, Cr, Mn and V were recorded for S_4 , S_5 , S_{11} , S_1 and S_{15} , respectively. The higher concentration of these elements may be due to the environment of Ti, V and Cr in minerals such as ilmenite, rutile and chromite present in the samples. This may be due to heavy minerals present in the samples and also in sediments^[22]. The low concentration of Co in the present study shows that its mobility is reduced in the carbonate dominant environment^[23]. Another reason for dilution may be wind and fluvial material brought in by the streams in the study area and also this implies that the sediment is free from this metal pollution. The presence of Zr and Hf in the study indicates the possibility of heavy minerals present in the sediment. In beach rock samples, the contents of REEs follow the order Ce>La>Sm>Yb. This is consistent with average abundance in the earth's crust.

The variation of the different trace elements in the present study may be due to the nature of weathering processes, and the velocity of transporting media. The total trace elements concentrations in sediments depend not only on the trace element input but also on the mineral composition of the sediment, which can be different from area to area.

4 Conclusion

(1)The FT-IR and XRD techniques confirm the cementation of beach rock samples caused by calcite and aragonite and also revealed the presence of various minerals in the samples.

(2)The radioactivity analysis indicates that Vattakottai (S_{15}) is the highest zone of radioactivity.

(3)The elemental analysis shows Vattakottai having the high abundance of heavy metals and trace elements.

(4)High concentration radioactive element, trace elements and heavy metal in a few sampling sites of the study area may be ascribed primarily to the reworking of heavy mineral laden quaternary sediments in the coastal plains that probably extend offshore and onshore movements and long shore currents.

(5)Among the sites vattakottai site (S_{15}) draws attention as it registers largest accumulation of heavy minerals, heavy metals and trace elements.

(6)The combined use of mineralogical, multi-elemental and radioactivity measurement is an adequate methodology to identify the source of pollution in the area.

(7)Data on the radioactive and stable trace elements can be utilized in possible exploitation of these minerals in the study area. From the environmental protection point of view, the study area is free from any radiological hazard.

(8) This study demonstrates feasibility of spectroscopy and INAA analysis in beach rock samples and it is proven that the techniques can be used for environmental matrix.

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